

## FLAME RETARDANT COMPOSITION COMPRISING A PHOSPHONIC ACID METAL SALT AND A NITROGEN-CONTAINING COMPOUND

The invention relates to a novel flame retardant combination and to the use thereof in synthetic, especially thermoplastic, polymers.

Metal salts of phosphonic acids, on their own or in combination with other components, are known as flame retardants for a large number of thermoplastic polymers, for example from GB-A-2 211 850, EP-A-245 207, EP-A-343 109 and DE-A-3 833 977, wherein special emphasis is to be given to the salts of the methyl ester of methyl phosphonic acid.

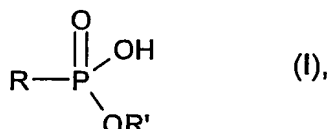
Nitrogen-containing flame retardants, especially those based on melamine, have been known for a long time and are, in some cases, commercially available. Some of those melamine derivatives also contain phosphorus. Examples of publications relating to such flame retardants are, *inter alia*, EP-A-782 599, EP-A-1 095 030, US-A-4 010 137 and US-A-3 915 777.

Combinations of nitrogen-containing flame retardants with flame retardants based on phosphorus compounds are also known. In that respect see, for example, DE-A-197 34 437, DE-A-197 37 727, WO-A-97/39053, EP-A-1 070 754, EP-A-6568 and DE-A-196 14 424.

There is a continuing need for flame retardants that have improved properties and that can be used in various plastics. In particular, increased safety and environmental requirements mean that hitherto known flame retardants are no longer capable of satisfying all demands.

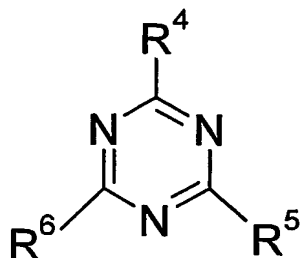
It has now been found that the combined use of nitrogen-containing flame retardants, especially those based on melamine, with salts of alkyl- or aryl-phosphonic acids, delivers outstanding action in a number of polymers.

The invention accordingly relates to a flame retardant comprising  
A. at least one metal or metalloid salt of a phosphonic acid of formula I

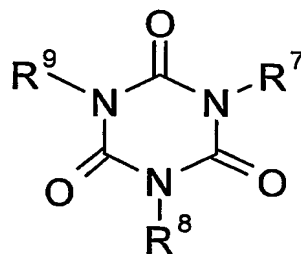


wherein R is hydrogen, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>5</sub>-C<sub>6</sub>cycloalkyl, C<sub>2</sub>-C<sub>6</sub>alkenyl, C<sub>6</sub>-C<sub>10</sub>aryl or C<sub>7</sub>-C<sub>11</sub>aralkyl and R' is hydrogen, C<sub>1</sub>-C<sub>8</sub>alkyl, C<sub>6</sub>-C<sub>10</sub>aryl or C<sub>7</sub>-C<sub>11</sub>aralkyl, the substituents R and R' that are other than hydrogen being unsubstituted or substituted by halogen, hydroxyl, amino, C<sub>1</sub>-C<sub>4</sub>alkylamino, di-C<sub>1</sub>-C<sub>4</sub>alkylamino, C<sub>1</sub>-C<sub>4</sub>alkoxy, carboxy or C<sub>2</sub>-C<sub>5</sub>alkoxycarbonyl; and the metal or metalloid is from Group IA, IB, IIA, IIB, IIIA, IVA, VA or VIII of the Periodic Table; and

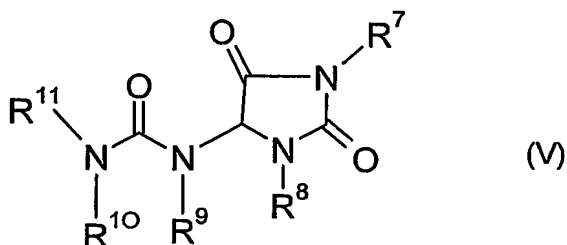
B. at least one nitrogen-containing flame retardant component of formulae III to VIIIa



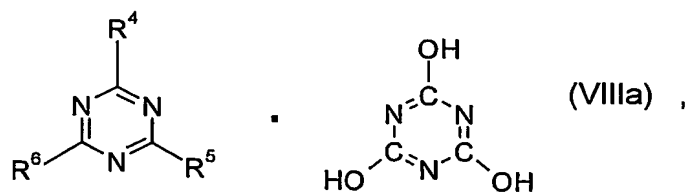
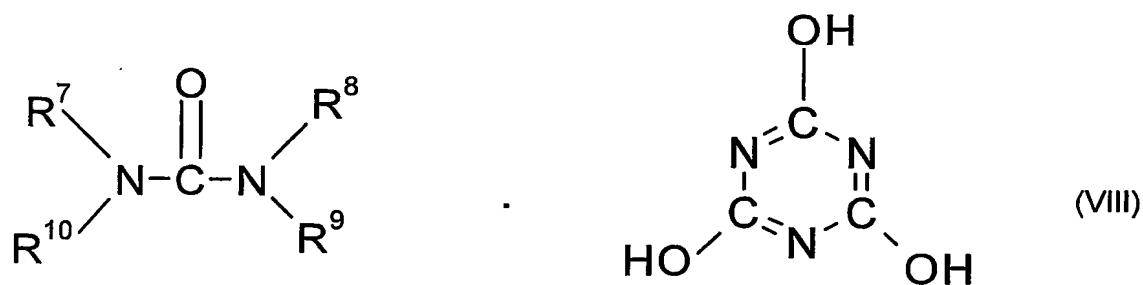
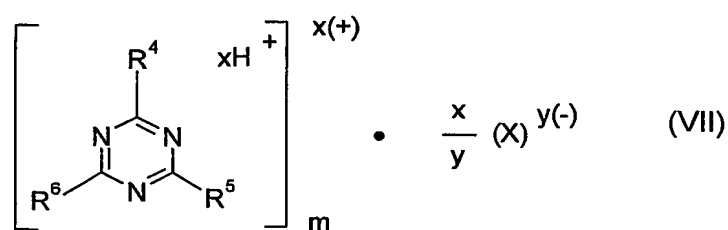
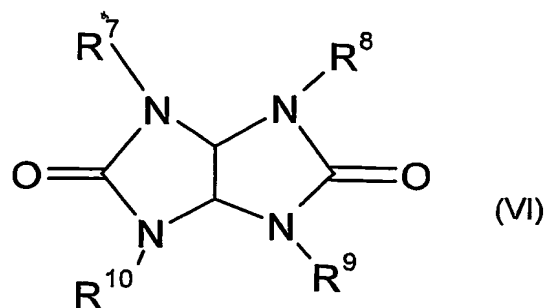
(III)



(IV)



(M)



wherein

R<sup>4</sup> to R<sup>6</sup> are each independently of the others hydrogen, C<sub>1</sub>-C<sub>8</sub>alkyl, C<sub>5</sub>-C<sub>6</sub>cycloalkyl or C<sub>1</sub>-C<sub>4</sub>alkyl-C<sub>5</sub>-C<sub>6</sub>cycloalkyl, each unsubstituted or substituted by a hydroxy or C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl group; C<sub>2</sub>-C<sub>8</sub>alkenyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, -acyl, -acyloxy, C<sub>6</sub>-C<sub>12</sub>aryl, -O-R<sup>2</sup> or -N(R<sup>2</sup>)R<sup>3</sup>, and R<sup>2</sup> and R<sup>3</sup> are hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>5</sub>-C<sub>6</sub>cycloalkyl, C<sub>2</sub>-C<sub>8</sub>alkenyl,

C<sub>1</sub>-C<sub>4</sub>hydroxyalkyl or C<sub>6</sub>-C<sub>12</sub>aryl, with the proviso that R<sup>4</sup> to R<sup>6</sup> are not simultaneously hydrogen and also, in formula III, not simultaneously -NH<sub>2</sub>, and in formula VII at least one group is present which is capable of adding a proton,

R<sup>7</sup> to R<sup>11</sup> each independently of the others have the same possible meanings as R<sup>4</sup> to R<sup>6</sup> with the exception of -N(R<sup>2</sup>)R<sup>3</sup>, X is the anion of a protonic acid, x is the number of protons transferred from the latter to the triazine compound and y is the number of protons abstracted from the protonic acid;

or ammonium polyphosphate, a melamine ammonium phosphate, a melamine ammonium polyphosphate, melamine ammonium pyrophosphate, a condensation product of melamine or/and a reaction product of melamine with phosphoric acid or/and a reaction product of a condensation product of melamine with phosphoric acid or mixtures thereof.

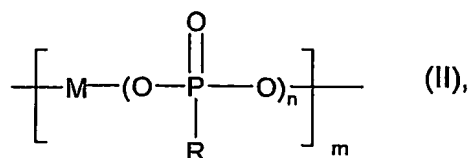
In formula I, alkyl groups R and R' contain preferably from 1 to 8, for example from 1 to 6, especially from 1 to 4, carbon atoms. Aryl groups are preferably naphthyl and especially phenyl. Aralkyl is especially phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl or naphthylmethyl, more especially benzyl or phenylethyl. When such groups R or R' are further substituted, they carry especially from 1 to 3 of the substituents mentioned.

Special preference is given to R being C<sub>1</sub>-C<sub>3</sub>alkyl and R' being hydrogen or methyl.

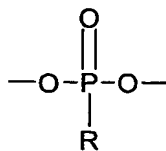
Examples of the metal are Na, K, Mg, Ca, Ba, Zn, B, Al, Cu, Fe, Sn or Sb, especially Mg or Al, more especially the latter.

The salts may be present as simple ionic compounds comprising the anions of phosphonic acid and the cations of the metal or metalloid.

When R' is hydrogen and the metal or metalloid has a valency of more than one, the salt can have a polymeric structure according to the following formula II

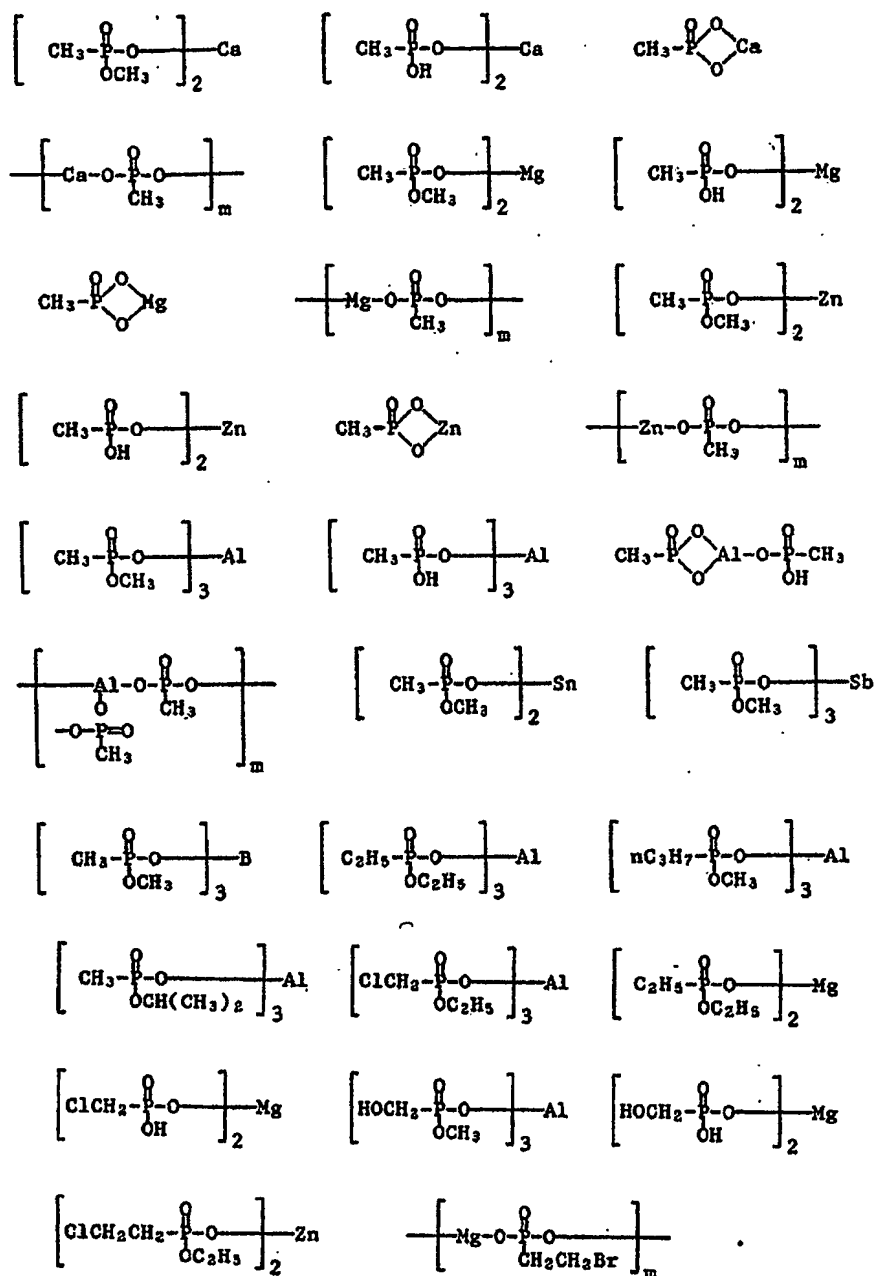


wherein R is as defined hereinbefore, M is a metal or metalloid, n has a value corresponding to the valency of M minus 1, m is a number from 2 to 100 and wherein each group



is bonded only to M atoms.

As examples of phosphonic acid salts that may be used in accordance with the invention there may be mentioned:



The phosphonic acid salts according to the definition either are known or can be prepared in accordance with methods known *per se*. Examples of such methods are to be found in, *inter alia*, EP-A-245 207, pages 4 and 5 to 7 (Examples 1 to 14).

The symbol X in formula VII denotes, for example, an anion of phosphoric acid, polyphosphoric acid (linear or branched), pyrophosphoric acid, phosphinic acid, phosphonic acid or boric acid.

$R^4$  to  $R^6$  are, for example, each independently of the others, hydrogen,  $C_1$ - $C_4$ alkyl, cyclopentyl, cyclohexyl, methylcyclohexyl,  $C_1$ - $C_4$ hydroxyalkyl,  $C_2$ - $C_6$ alkenyl,  $C_1$ - $C_4$ alkoxy, phenyl which is unsubstituted or substituted by from 1 to 3 methyl or methoxy groups or/and by halogen atoms,  $-OR^2$  or  $-NR^2R^3$ , wherein  $R^2$  and  $R^3$  are each independently of the other hydrogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ hydroxyalkyl, cycloalkyl, methylcyclohexyl or phenyl which is unsubstituted or substituted by from 1 to 3 methyl or methoxy groups or/and halogen atoms. In formula III, preference is given to at least one of  $R^2$  and  $R^3$  being other than hydrogen.

For  $R^7$  to  $R^{11}$  the same preferences as for  $R^4$  to  $R^6$  also apply by analogy.

As component B there are advantageously used compounds of formulae IV, V, VI, VII, VIII and VIIa and also the melamine compounds specifically mentioned, especially the compounds of formulae VII, VIIa and also the melamine compounds specifically mentioned.

Preferred nitrogen compounds (component B) are, for example, benzoguanamine (formula III,  $R^4$  = phenyl,  $R^5$  =  $R^6$  =  $-NH_2$ ), tris(hydroxyethyl) isocyanurate (formula IV,  $R^7$  =  $R^8$  =  $R^9$  =  $-CH_2-CH_2-OH$ ), allantoin (formula V,  $R^7$  =  $R^8$  =  $R^9$  =  $R^{10}$  =  $R^{11}$  = H), glycoluril (formula VI,  $R^7$  =  $R^8$  =  $R^9$  =  $R^{10}$  = H) and also melamine phosphate, dimelamine phosphate and melamine pyrophosphate, melamine polyphosphate, melamine borate (all of formula VII type), urea cyanurate (formula VIII type), melamine cyanurate (formula VIIa type), and also melam or melem phosphate, melam or melem polyphosphate, ammonium polyphosphate, melamine ammonium phosphate, pyrophosphate or polyphosphate.

The compounds used as component B are known or can be obtained by known customary methods. Some of them are commercially available.

Special emphasis should be given to flame retardants according to the invention wherein, in component A, R is  $C_1$ - $C_4$ alkyl which is unsubstituted or substituted by from 1 to 3 halogen atoms or/and hydroxyl groups and  $R'$  is hydrogen or  $C_1$ - $C_4$ alkyl, especially those wherein R is

C<sub>1</sub>-C<sub>3</sub>alkyl and R' is hydrogen or C<sub>1</sub>-C<sub>3</sub>alkyl, and more especially those wherein R and R' are each methyl and the metal is Al.

Advantageously, component B in the flame retardants is benzoguanamine, tris(hydroxyethyl) isocyanurate, allantoin, glycoluril, melamine cyanurate, melamine phosphate, dimelamine phosphate, melamine pyrophosphate, urea cyanurate, melamine polyphosphate, melamine borate, ammonium polyphosphate, melamine ammonium polyphosphate or melamine ammonium pyrophosphate, preferably a condensation product of melamine from the series melem, melam, melon and/or a higher condensed compound or a reaction product of melamine with phosphoric acid and/or a reaction product of condensation products of melamine with phosphoric acid or a mixture thereof. Special emphasis should be given to: dimelamine pyrophosphate, melamine polyphosphate, melem polyphosphate, melam polyphosphate, and/or a mixed polysalt of such a type, more especially melamine polyphosphate.

The ratio of components A and B may vary within wide limits and is dependent upon the intended use. Examples of ratios A:B are from 5:95 to 95:5, e.g. from 10:90 to 90:10, preferably from 20:80 to 80:20, especially from 30:70 to 70:30 and from 40:60 to 60:40.

Both component A and component B may comprise one or more compounds of formula I or/and II or of formulae III to VIIIa or the melamine compounds specifically mentioned, mixtures of compounds of different formulae being possible.

The flame retardants according to the invention are outstandingly suitable for imparting flame-retarding properties to synthetic polymers, especially thermoplastics.

Examples of such synthetic polymers are:

1. Polymers of mono- and di-olefins, for example polypropylene, polyisobutylene, polybutene-1, poly-4-methylpentene-1, polyvinylcyclohexane, polyisoprene or polybutadiene and also polymerisates of cyclo-olefins, for example of cyclopentene or norbornene; and also polyethylene (which may optionally be crosslinked), for example high density polyethylene (HDPE), high density polyethylene of high molecular weight (HDPE-HMW), high density polyethylene of ultra-high molecular weight (HDPE-UHMW), medium density polyethylene



(MDPE), low density polyethylene (LDPE), and linear low density polyethylene (LLDPE), (VLDPE) and (ULDPE).

Polyolefins, that is to say polymers of mono-olefins, as mentioned by way of example in the preceding paragraph, especially polyethylene and polypropylene, can be prepared by various processes, especially by the following methods:

- a) by free radical polymerisation (usually at high pressure and high temperature);
- b) by means of a catalyst, the catalyst usually containing one or more metals of group IVb, Vb, VIb or VIII. Those metals generally have one or more ligands, such as oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls, which may be either  $\pi$ - or  $\sigma$ -coordinated. Such metal complexes may be free or fixed to carriers, for example to activated magnesium chloride, titanium(III) chloride, aluminium oxide or silicon oxide. Such catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be active as such in the polymerisation or further activators may be used, for example metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyl oxanes, the metals being elements of group(s) Ia, IIa and/or IIIa. The activators may have been modified, for example, with further ester, ether, amine or silyl ether groups. Such catalyst systems are usually referred to as Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or Single Site Catalysts (SSC).

2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).

3. Copolymers of mono- and di-olefins with one another or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/butene-1 copolymers, propylene/isobutylene copolymers, ethylene/butene-1 copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, ethylene/vinylcyclohexane copolymers, ethylene/cyclo-olefin copolymers, for example ethylene/norbornene (COC), ethylene/1-olefin copolymers wherein the 1-olefin is

prepared *in situ*, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/vinyl cyclohexene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers, ethylene/acrylic acid copolymers and salts thereof (ionomers), and also terpolymers of ethylene with propylene and a diene, such as hexadiene, dicyclopentadiene or ethylidenenorbornene; and also mixtures of such copolymers with one another or with polymers mentioned under 1), for example polypropylene-ethylene/propylene copolymers, LDPE-ethylene/vinyl acetate copolymers, LDPE-ethylene/acrylic acid copolymers, LLDPE-ethylene/vinyl acetate copolymers, LLDPE-ethylene/acrylic acid copolymers and alternately or randomly structured polyalkylene-carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

4. Polystyrene, poly(p-methylstyrene), poly( $\alpha$ -methylstyrene).

5. Aromatic homopolymers and copolymers derived from vinyl-aromatic monomers, for example styrene,  $\alpha$ -methylstyrene, all isomers of vinyltoluene, for example p-vinyltoluene, all isomers of ethylstyrene, propylstyrene, vinylbiphenyl, vinylnaphthalene, vinylanthracene and mixtures thereof; homopolymers and copolymers can have a syndiotactic, isotactic, hemi-isotactic or atactic stereo structure; preference is given to atactic polymers. Also included are stereoblock polymers.

6a. Copolymers including the already mentioned vinyl-aromatic monomers and comonomers selected from ethylene, propylene, dienes, nitriles, acids, maleic anhydrides, maleic acid amides, vinyl acetate, vinyl chloride and acrylic acid derivatives and mixtures thereof, for example styrene/butadiene, styrene/acrylonitrile, styrene/ethylene (interpolymers), styrene/alkyl methacrylate, styrene/butadiene/alkyl acrylate and methacrylate, styrene/maleic anhydride, styrene/acrylonitrile/methyl acrylate; high-impact-strength mixtures consisting of styrene copolymers and another polymer, for example a polyacrylate, a diene polymer or an ethylene/propylene/diene terpolymer; and also block copolymers of styrene, for example styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene-butylene/styrene or styrene/ethylene-propylene/styrene.

6b. Hydrogenated aromatic polymers prepared by hydrogenation of the polymers mentioned under 6.), especially polycyclohexylethylene (PCHE), often also referred to as polyvinylcyclohexane (PVCH), which is prepared by hydrogenation of atactic polystyrene.

6c. Hydrogenated aromatic polymers prepared by hydrogenation of the polymers mentioned under 6a.).

Homopolymers and copolymers can have a syndiotactic, isotactic, hemi-isotactic or atactic stereo structure; preference is given to atactic polymers. Also included are stereoblock polymers.

7. Graft copolymers of vinyl-aromatic monomers, for example styrene on polybutadiene, styrene on polybutadiene/styrene or polybutadiene/acrylonitrile copolymers, styrene and acrylonitrile (or methacrylonitrile) on polybutadiene; styrene, acrylonitrile and methyl methacrylate on polybutadiene; styrene and maleic anhydride on polybutadiene; styrene, acrylonitrile and maleic anhydride or maleic acid imide on polybutadiene; styrene and maleic acid imide on polybutadiene, styrene and alkyl acrylates or alkyl methacrylates on polybutadiene, styrene and acrylonitrile on ethylene/propylene/diene terpolymers, styrene and acrylonitrile on polyalkyl acrylates or polyalkyl methacrylates, styrene and acrylonitrile on acrylate/butadiene copolymers, and mixtures thereof with the copolymers mentioned under 6), such as those known, for example, as so-called ABS, MBS, ASA or AES polymers.

8. Halogen-containing polymers, for example polychloroprene, chlorinated rubber, chlorinated and brominated copolymer of isobutylene/isoprene (halobutyl rubber), chlorinated or chlorosulfonated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin homo- and co-polymers, especially polymers of halogen-containing vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride; and copolymers thereof, such as vinyl chloride/vinylidene chloride, vinyl chloride/vinyl acetate or vinylidene chloride/vinyl acetate.

9. Polymers derived from  $\alpha,\beta$ -unsaturated acids and derivatives thereof, such as polyacrylates and polymethacrylates, or polymethyl methacrylates, polyacrylamides and polyacrylonitriles impact-resistant-modified with butyl acrylate.

10. Copolymers of the monomers mentioned under 9) with one another or with other unsaturated monomers, for example acrylonitrile/butadiene copolymers, acrylonitrile/alkyl acrylate copolymers, acrylonitrile/alkoxyalkyl acrylate copolymers, acrylonitrile/vinyl halide copolymers or acrylonitrile/alkyl methacrylate/butadiene terpolymers.
11. Polymers derived from unsaturated alcohols and amines or their acyl derivatives or acetals, such as polyvinyl alcohol, polyvinyl acetate, stearate, benzoate or maleate, polyvinylbutyral, polyallyl phthalate, polyallylmelamine; and the copolymers thereof with olefins mentioned in Point 1.
12. Homo- and co-polymers of cyclic ethers, such as polyalkylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.
13. Polyacetals, such as polyoxymethylene, and also those polyoxymethylenes which contain comonomers, for example ethylene oxide; polyacetals modified with thermoplastic polyurethanes, acrylates or MBS.
14. Polyphenylene oxides and sulfides and mixtures thereof with styrene polymers or polyamides.
15. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, such as polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides derived from m-xylene, diamine and adipic acid; polyamide 6/I (polyhexamethylene isophthalamide, MXD (m-xylylenediamine); polyamides prepared from hexamethylenediamine and iso- and/or tere-phthalic acid and optionally an elastomer as modifier, for example poly-2,4,4-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide. Block copolymers of the above-mentioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with polyethers, for example with polyethylene glycol, polypropylene glycol or polytetramethylene glycol. Also polyamides or copolyamides modified with EPDM or ABS; and polyamides condensed during processing ("RIM polyamide systems").

Examples of polyamides and copolyamides that can be used are derived from, *inter alia*,  $\epsilon$ -caprolactam, adipic acid, sebacic acid, dodecanoic acid, isophthalic acid, terephthalic acid, hexamethylenediamine, tetramethylenediamine, 2-methyl-pentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, 2,4,4-trimethylhexamethylenediamine, m-xylylenediamine or bis(3-methyl-4-aminocyclohexyl)methane;

and also semi-aromatic polyamides such as polyamide 66/6I, for example consisting of 70 - 95 % polyamide 6/6 and 5 - 30 % polyamide 6/I; and also tricopolymers in which some of the polyamide 6/6 has been replaced, for example consisting of 60 - 89 % polyamide 6/6, 5 - 30 % polyamide 6/I and 1 - 10 % of another aliphatic polyamide; the latter may consist of, for example, polyamide 6, polyamide 11, polyamide 12 or polyamide 6/12 units. Such tricopolymers may accordingly be designated polyamide 66/6I/6, polyamide 66/6I/11, polyamide 66/6I/12, polyamide 66/6I/6I0 or polyamide 66/6I/6I2.

16. Polyureas, polyimides, polyamide imides, polyether imides, polyester imides, polyhydantoins and polybenzimidazoles.

17. Polyesters derived from dicarboxylic acids and dialcohols and/or from hydroxycarboxylic acids or the corresponding lactones, such as polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylolcyclohexane terephthalate, polyalkylene naphthalate (PAN) and polyhydroxybenzoates, and also block polyether esters derived from polyethers with hydroxyl terminal groups; and also polyesters modified with polycarbonates or MBS.

18. Polycarbonates and polyester carbonates.

19. Polyketones

20. Polysulfones, polyether sulfones and polyether ketones.

21. Mixtures (polyblends) of the afore-mentioned polymers, for example PP/EPDM, polyamide/EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR, POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA 6.6 and copolymers, PA/HDPE, PA/PP, PA/PPO, PBT/PC/ABS or PBT/PET/PC.

The present invention accordingly relates also to the use of the flame retardants according to the invention in imparting flame-resistant properties to synthetic polymers, especially to thermoplastics, and also to a method of imparting flame-resistant properties to synthetic polymers, wherein at least one flame retardant according to the invention is incorporated in the synthetic polymers or is applied to their surface.

The invention relates also to a composition comprising

- a) a synthetic polymer and
- b) a flame retardant according to the invention, the synthetic polymer preferably being a thermoplastic polymer.

Preference is given to compositions wherein the thermoplastic polymer is high-impact polystyrene (HIPS), expandable polystyrene (EPS), expanded polystyrene (XPS), polyphenylene ether (PPE), polyamide, polyester, polycarbonate (PC) or a polymer blend of the type ABS (acrylonitrile-butadiene-styrene) or PC/ABS (polycarbonate/acrylonitrile-butadiene-styrene) or PPE/HIPS (polyphenylene ether/high-impact polystyrene), especially a polyamide, polyester or a PPE/HIPS blend.

Special preference is given to polymer compositions according to the invention that comprise a filler or a reinforcing agent, especially glass-fibre-reinforced polymers, e.g. glass-fibre-reinforced polyamide.

Preparation of the compositions according to the invention may be carried out either by adding or applying the flame retardants consisting of components A and B according to the invention or, however, by adding or applying the individual components A and B separately.

Preference is given to the use of components A and B, each independently of the other, in a concentration of from 1 to 30 % by weight, for example from 3 to 20 % by weight, preferably from 3 to 15 % by weight, based on the plastics moulding material.

The compositions according to the invention contain the flame retardant consisting of components A and B in an amount of, for example, from 1 to 50 % by weight, preferably from

3 to 40 % by weight, especially from 3 to 30 % by weight or from 8 to 30 % by weight, based on the composition.

The flame-retarding components A and B may be incorporated in the polymers, for example by pre-mixing all the constituents in the form of powder and/or granules in a mixer and then homogenising in the polymer melt in a compounding unit (*inter alia*, a twin-screw extruder). The melt is usually drawn off in the form of an extrudate, cooled and granulated. Components A and B may also be directly introduced separately into the compounding unit by means of a feed unit.

It is likewise possible for the flame-retarding components A and B to be admixed with finished polymer granules or powder and the mixture immediately processed into moulded articles using an injection-moulding machine. In the case of polyesters, for example, the flame-retarding additives A and B may also already be added to the polyester material during polycondensation.

The polymer compositions according to the invention may be in the form of moulding materials, films, fibres and other moulded articles or in the form of surface-coating compositions or may be further processed into such forms.

It can be advantageous for the flame retardants according to the invention to be processed into a stable product form before addition to the polymer(s) in question to produce the polymer compositions according to the invention. This may serve the purpose, on the one hand, of better meterability and better industrial hygiene (e.g. freedom from dust) and, on the other hand, of a stable form for marketing. Preferred product forms of the latter kind are, for example, granules and agglomerates. The former can be obtained, for example, by extruding mixtures from an extruder and granulating the extrudate. Alternatively, the mixture can be heated to above the melting point and the melt solidified by conventional methods (e.g. dripping onto a cooling belt or into a liquid such as water or spraying into air). In such methods the flame retardant mixture according to the invention may be processed as such or after addition of a carrier or of another adjuvant, for example a wax, plasticiser etc.. Examples of the methods mentioned can be found in, for example, EP-A-392 392 and EP-A-565 184.

To produce agglomerates, for example, an organic adjuvant, for example a polyvinyl alcohol, polyvinylpyrrolidone or polyvinylcaprolactam, is added to a mixture of the flame retardant according to the invention and then spray-dried. By that means, a free-flowing, dust-free agglomerate is obtained. It can be obtained, for example, analogously to the method described in WO-A-03/035736.

The flame-resistant polymer compositions are suitable, *inter alia*, for the production of moulded articles, films, threads and fibres, for example by injection-moulding, extrusion or compression-moulding.

In addition to the flame-retarding combination of A and B according to the invention, further customary components, for example fillers and reinforcing agents such as glass fibres, glass beads or minerals such as chalk, may be added to the polymer compositions. In addition, other additives such as antioxidants, light stabilisers, lubricants, colorants, nucleating agents or antistatics may be included.

Examples of further additives optionally present in the compositions according to the invention are:

### 1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-( $\alpha$ -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, linear nonylphenols or nonylphenols branched in the side-chain, e.g. 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)-phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol.



1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example  $\alpha$ -tocopherol,  $\beta$ -tocopherol,  $\gamma$ -tocopherol,  $\delta$ -tocopherol and mixtures thereof (Vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulfide.

1.6. Alkylidene bisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-( $\alpha$ -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-( $\alpha$ -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-( $\alpha,\alpha$ -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl] terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzyl mercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzyl mercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-

tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzyl mercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl 2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, dioctadecyl 2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecylmercaptoethyl 2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, di-[4-(1,1,3,3-tetramethylbutyl)phenyl] 2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Hydroxybenzyl aromatic compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine compounds, for example 2,4-bis(octylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate.

1.11. Benzylphosphonates, for example dimethyl 2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, calcium salt of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid monoethyl ester.

1.12. Acylaminophenols, for example 4-hydroxylauric acid anilide, 4-hydroxystearic acid anilide, N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamic acid octyl ester.

1.13. Esters of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or poly-hydric alcohols, for example with methanol, ethanol, n-octanol, isooctanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate,

N,N'-bis(hydroxyethyl)oxalic acid diamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.14. Esters of  $\beta$ -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, for example with methanol, ethanol, n-octanol, isooctanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalic acid diamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; 3,9-bis[2-{3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane.

1.15. Esters of  $\beta$ -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, for example with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalic acid diamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenylacetic acid with mono- or polyhydric alcohols, for example with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalic acid diamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.17. Amides of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, for example N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazide), N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]-propionyloxy)ethyl]-oxamide (Naugard®XL-1 from Uniroyal).

1.18. Ascorbic acid (Vitamin C).

1.19. Amine-type antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethyl-butyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfonamido)-diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyl-diphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, di(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-di[(2-methylphenyl)amino]ethane, 1,2-di(phenylamino)propane, (o-tolyl)-biguanide, di[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, mixture of mono- and di-alkylated tert-butyl-/tert-octyl-diphenylamines, mixture of mono- and di-alkylated nonyl-diphenylamines, mixture of mono- and di-alkylated dodecyldiphenylamines, mixture of mono- and di-alkylated isopropyl-/isohexyl-diphenylamines, mixtures of mono- and di-alkylated tert-butyl-diphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, mixture of mono- and di-alkylated tert-butyl-/tert-octyl-phenothiazines, mixture of mono- and di-alkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperid-4-yl)-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl) sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

## 2. UV absorbers and light stabilisers

2.1. 2-(2'-Hydroxyphenyl)-benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)-benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)-phenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)-benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)-benzotriazole, 2-(3',5'-di-tert-amyl-2'-

hydroxyphenyl)-benzotriazole, 2-(3',5'-bis( $\alpha,\alpha$ -dimethylbenzyl)-2'-hydroxyphenyl)-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)-phenyl)-benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-yl-phenol]; transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-benzotriazole with polyethylene glycol 300;

$\left[ \text{R}-\text{CH}_2\text{CH}_2-\text{COO}-\text{CH}_2\text{CH}_2 \right]_2$  wherein R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-yl-phenyl; 2-[2'-hydroxy-3'-( $\alpha,\alpha$ -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)-phenyl]-benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-( $\alpha,\alpha$ -dimethylbenzyl)-phenyl]-benzotriazole.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyl-oxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy or 2'-hydroxy-4,4'-dimethoxy derivative.

2.3. Esters of unsubstituted or substituted benzoic acids, for example 4-tert-butyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoylresorcinol, 3,5-di-tert-butyl-4-hydroxybenzoic acid 2,4-di-tert-butylphenyl ester, 3,5-di-tert-butyl-4-hydroxybenzoic acid hexadecyl ester, 3,5-di-tert-butyl-4-hydroxybenzoic acid octadecyl ester, 3,5-di-tert-butyl-4-hydroxybenzoic acid 2-methyl-4,6-di-tert-butylphenyl ester.

2.4. Acrylates, for example  $\alpha$ -cyano- $\beta,\beta$ -diphenylacrylic acid ethyl ester or isooctyl ester,  $\alpha$ -methoxycarbonylcinnamic acid methyl ester,  $\alpha$ -cyano- $\beta$ -methyl-p-methoxycinnamic acid methyl ester or butyl ester,  $\alpha$ -methoxycarbonyl-p-methoxycinnamic acid methyl ester, N-( $\beta$ -methoxycarbonyl- $\beta$ -cyanovinyl)-2-methyl-indoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thio-bis[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, optionally with additional ligands, such

as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyl dithiocarbamate, nickel salts of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid monoalkyl esters, such as of the methyl or ethyl ester, nickel complexes of ketoximes, such as of 2-hydroxy-4-methylphenylundecyl ketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, optionally with additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethylpiperid-4-yl) sebacate, bis(2,2,6,6-tetramethylpiperid-4-yl) succinate, bis(1,2,2,6,6-pentamethylpiperid-4-yl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperid-4-yl) sebacate, n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonic acid bis(1,2,2,6,6-pentamethylpiperidyl) ester, condensation product of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensation products of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl) nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetraoate, 1,1'-(1,2-ethanediy)bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyl-oxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl) malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) succinate, linear or cyclic condensation products of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, condensation product of 2-chloro-4,6-di(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, condensation product of 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, mixture of 4-hexadecyloxy- and 4-stearyl-oxy-2,2,6,6-tetramethylpiperidine, condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine and 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); condensation product of 1,6-diaminohexane and 2,4,6-trichloro-1,3,5-triazine and also N,N-dibutylamine and 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [192268-64-7]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4.5]decane,

reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro-[4.5]decane and epichlorohydrin, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyloxycarbonyl)-2-(4-methoxyphenyl)ethene, N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, diester of 4-methoxymethylenemalonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane, reaction product of maleic anhydride  $\alpha$ -olefin copolymer and 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

2.7. Oxalic acid diamides, for example 4,4'-dioctyloxy oxanilide, 2,2'-diethoxy oxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butyl oxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butyl oxanilide, 2-ethoxy-2'-ethyl oxanilide, N,N'-bis(3-dimethylaminopropyl) oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyl oxanilide and a mixture thereof with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyl oxanilide, mixtures of o- and p-methoxy- and also of o- and p-ethoxy-di-substituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-[2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

3. Metal deactivators, for example N,N'-diphenyloxalic acid diamide, N-salicylal-N'-salicyloylhydrazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalic acid dihydrazide, oxanilide, isophthalic acid dihydrazide, sebacic acid bis-phenylhydrazide, N,N'-diacetyl adipic

acid dihydrazide, N,N'-bis-salicyloyloxalic acid dihydrazide, N,N'-bis-salicyloylthiopropionic acid dihydrazide.

4. Phosphites and phosphonites, e.g. triphenyl phosphite, diphenylalkyl phosphites, phenyl-dialkyl phosphites, tris(nonylphenyl)phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl-pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl)phosphite, diisodecylpentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,4-dicumylphenyl)-pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, bis-isodecyloxy-pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tri-tert-butylphenyl)pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocine, bis(2,4-di-tert-butyl-6-methylphenyl) methylphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethylphosphite, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[d,g]-1,3,2-dioxaphosphocine, 2,2',2''-nitrido[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)-phosphite], 2-ethylhexyl-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite, 5-butyl-5-ethyl-2-(2,4,6-tri-tert-butylphenoxy)-1,3,2-dioxaphosphirane.

5. Hydroxylamines, for example N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-diethylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine from hydrogenated tallow fatty amines.

6. Nitrones, for example N-benzyl-alpha-phenylnitron, N-ethyl-alpha-methylnitron, N-octyl-alpha-heptylnitron, N-lauryl-alpha-undecylnitron, N-tetradecyl-alpha-tridecylnitron, N-hexadecyl-alpha-pentadecylnitron, N-octadecyl-alpha-heptadecylnitron, N-hexadecyl-alpha-heptadecylnitron, N-octadecyl-alpha-pentadecylnitron, N-heptadecyl-alpha-heptadecylnitron, N-octadecyl-alpha-hexadecylnitron, nitrones derived from N,N-dialkylhydroxylamines prepared from hydrogenated tallow fatty amines.

7. Thiosynergistic compounds, for example thiodipropionic acid dilauryl ester or thiodipropionic acid distearyl ester.



8. Peroxide-destroying compounds, for example esters of  $\beta$ -thio-dipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl ester, mercaptobenzimidazole, the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyldisulfide, pentaerythritol tetrakis( $\beta$ -dodecylmercapto)propionate.

9. Polyamide stabilisers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

10. Basic co-stabilisers, for example melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate, potassium palmitate, antimony pyrocatecholate or zinc pyrocatecholate.

11. Nucleating agents, for example inorganic substances, e.g. talc, metal oxides, such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of preferably alkaline earth metals; organic compounds, such as mono- or poly-carboxylic acids and their salts, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds, for example ionic copolymerisates ("ionomers"). Special preference is given to 1,3:2,4-bis(3',4'-dimethylbenzylidene)sorbitol, 1,3:2,4-di(paramethyldibenzylidene)sorbitol and 1,3:2,4-di(benzylidene)sorbitol.

12. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, glass beads, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood powders, and powders and fibres of other natural products, synthetic fibres.

13. Other additives, for example plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow improvers, optical brighteners, antistatics, blowing agents.

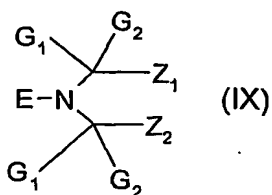
14. Benzofuranones and indolinones, for example as described in U.S. 4 325 863; U.S. 4 338 244; U.S. 5 175 312, U.S. 5 216 052; U.S. 5 252 643; DE-A-4 316 611; DE-A-4 316 622; DE-A-4 316 876; EP-A-0 589 839 or EP-A-0 591 102, or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)-

benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxy-phenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,4-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(2,3-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

Polymer compositions according to the invention additionally comprise, for example, antioxidants, processing stabilisers, light stabilisers, metal deactivators, hydroxylamines, thiosynergistic compounds, copper salts, nucleating agents, fillers, reinforcing agents, pigments and/or antistatics, especially phenolic or amine-type antioxidants, hydroxylamines, phosphites, phosphonites or/and benzofuranones and also, more especially, light stabilisers from the classes of UV absorbers or/and sterically hindered amines.

The flame retardants according to the invention and polymer compositions comprising them may also comprise further flame retardants (component C), for which any flame-retarding active ingredient from the classes known hitherto is, in principle, suitable. Examples are antimony compounds, for example antimony trioxide, antimony pentoxide or sodium antimonate, especially in combination with halogen compounds; alkaline earth metal oxides, for example magnesium oxide or other metal oxides such as zinc oxide, aluminium oxide, argillaceous earth, silica, iron oxide or manganese oxide; metal hydroxides, for example magnesium hydroxide or aluminium hydroxide; nanocomposites; mineral earths such as montmorillonite or kaolin; modified mineral earths, for example comprising primary or quaternary ammonium compounds, melamine or phosphorus-containing compounds; silicon-containing compounds, for example silicates, e.g. calcium silicate, organosilicon compounds (aliphatic or aromatic), for example silicones; titanates or zirconates; metal borates, for example zinc borate (hydrated or non-hydrated); other metal compounds such as calcium sulfate, magnesium carbonate, molybdenum trioxide; further phosphorus compounds, for example phosphates, phosphate esters, phosphonates, phosphinates, phosphines, phosphazenes, phosphine oxides or phosphites, amongst which preference is given to phosphates, phosphinates and phosphonates; sterically hindered alkoxyamine compounds; and organohalogen compounds.

Sterically hindered alkoxyamine compounds correspond, for example, to the formula



wherein  $G_1$  and  $G_2$  are each independently of the other  $C_1$ - $C_8$ alkyl or together are pentamethylene or hexamethylene, each being preferably  $C_1$ - $C_4$ alkyl, especially methyl,

$Z_1$  and  $Z_2$  are each methyl or  $Z_1$  and  $Z_2$  together are a bridging group, especially for completion of a 5- or 6-membered ring, preferably a piperidine ring, it being possible for the resulting N-heterocycle to be unsubstituted or substituted, for example by ester, ether, amide, amino, carboxy or urethane groups,

E is alkoxy, alkenyloxy, cycloalkoxy, aralkoxy, aryloxy or  $O-T-(OH)_b$  and T is  $C_1$ - $C_{18}$ alkylene,  $C_5$ - $C_{18}$ cycloalkylene,  $C_5$ - $C_{18}$ cycloalkenylene, or  $C_1$ - $C_4$ alkylene substituted by phenyl or by phenyl substituted by 1 or 2  $C_1$ - $C_4$ alkyl groups, and

b is 1, 2 or 3, with b not being greater than the number of carbon atoms in T and, when b is 2 or 3, each hydroxyl group being bonded to a different carbon atom.

E is preferably  $C_1$ - $C_{18}$ alkoxy,  $C_5$ - $C_6$ cycloalkoxy, or  $C_1$ - $C_{18}$ alkoxy substituted by from 1 to 3 OH groups.

Examples of sterically hindered alkoxyamines of formula IX can be found in US-A-4 983 737, US-A-5 047 489 and US-A-5 077 340, and also GB-A-2 373 507 (especially page 7, line 1 to page 31, line 1; page 48, line 10 to page 52, third line from the bottom) and WO-A-03/050175 (especially page 11, penultimate line to page 37, last line; page 54, line 9 to third last line; pages 61/62, compounds NOR1 to NOR12). The mentioned locations are to be considered as part of the present Application.

The organohalogen compounds optionally present in flame retardants according to the invention may belong to a very great variety of chemical classes. Examples thereof are halogenated aromatic compounds, for example halogenated benzenes, biphenyls; phenols, ethers or esters thereof; bisphenols, diphenyl oxides; aromatic carboxylic acids or polyacids,

anhydrides, amides or imides thereof; halogenated cycloaliphatic or polycycloaliphatic compounds; and also halogenated aliphatic compounds, for example halogenated paraffins, oligomers and polymers, alkyl phosphates and alkyl isocyanurates. Examples of the mentioned classes of compounds are known from the literature. In that respect, see, for example, US-A-4 579 906 (e.g. column 3, lines 30-41), US-A-5 393 812 and also "Plastics Additives Handbook", Ed. by H. Zweifel, 5<sup>th</sup> Ed., Hanser Publ., Munich 2001, pages 681-698).

Individual examples of such halogenated organic flame retardant components are: chloroalkyl phosphate esters (Antiblaze<sup>®</sup> AB-100, Fyrol<sup>®</sup>FR-2), tris(2-chloroethyl) phosphate, polybrominated diphenyl oxide (DE-60F, Great Lakes Corp.), decabromodiphenyl oxide (DBDPO, Saytex<sup>®</sup>120E), tris[3-bromo-2,2-bis(bromomethyl)propyl] phosphate (PB 370<sup>®</sup>, FMC Corp.), tris(2,3-dibromopropyl) phosphate, tris(2,3-dichloropropyl) phosphate, chlorendic acid, tetrachlorophthalic acid, tetrabromophthalic acid, bis(N,N'-hydroxyethyl)-tetrachloro-phenylenediamine, poly- $\beta$ -chloroethyl triphosphonate mixture, bis(2,3-dibromopropyl ether) of bisphenol A (PE68), brominated epoxy resin, ethylene bis(tetrabromophthalimide) (Saytex<sup>®</sup> BT-93), bis(hexachlorocyclopentadiene)cyclooctane (Dechlorane Plus<sup>®</sup>), chlorinated paraffins, octabromodiphenyl ether, hexachlorocyclopentadiene derivatives, 1,2-bis(tribromophenoxy)ethane (FF68O), tetrabromo-bisphenol A (Saytex<sup>®</sup> RB100), ethylene bis(dibromonorborene-dicarboximide) (Saytex<sup>®</sup> BN-451), bis(hexachlorocyclopentadiene)-cyclooctane, polytetrafluoroethylene (Teflon<sup>®</sup> GC), tris(2,3-dibromopropyl) isocyanurate, ethylene bis(tetrabromophthalimide).

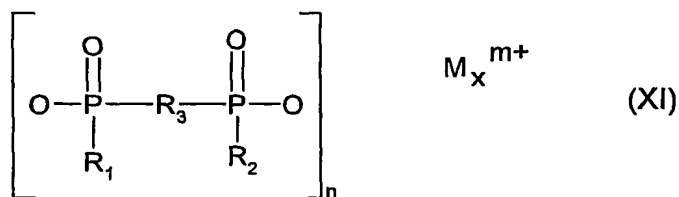
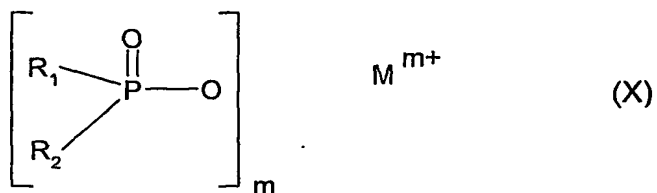
Among those, preference is given to organobromine flame retardants.

As examples of phosphorus-containing flame retardants there may be mentioned, for example:

tetraphenylresorcinol diphosphite (Fyroflex<sup>®</sup> RDP), triphenyl phosphate, trioctyl phosphate, tricresyl phosphate, tetrakis(hydroxymethyl)phosphonium sulfide, diethyl-N,N-bis(2-hydroxyethyl)aminomethyl phosphonate, hydroxyalkyl esters of phosphoric acids, ammonium polyphosphate (APP) or (Hostaflam<sup>®</sup> AP750), resorcinol diphosphate oligomer (RDP), phosphazene flame retardants and ethylenediamine diphosphate (EDAP).

The flame retardant component C from the class of phosphorus-containing flame retardants is advantageously a salt of melamine, or a condensation product thereof, with a phosphorus-containing acid, namely a monobasic phosphorus-containing acid, e.g. a phosphoric, phosphonic or, preferably, phosphinic acid having in each case only one acid equivalent; more especially, alkylphosphonic acid esters and, preferably, alkylphosphinic acid esters come into consideration. The cationic component is, for example, melamine, melam, melem or a higher condensation product of melamine, preferably melamine or melam. Such salts and their preparation are described, for example, in EP-A-363 321 and WO-A-01/57051.

Especially suitable as component C in flame retardants or flame-retarded polymer compositions according to the invention are salts of organic phosphinic acids or diphosphinic acids, especially salts of formulae X and XI



wherein

$\text{R}_1$  and  $\text{R}_2$ , which are the same or different, are  $\text{C}_1$ - $\text{C}_6$ alkyl, especially  $\text{C}_1$ - $\text{C}_4$ alkyl, or  $\text{C}_6$ - $\text{C}_{10}$ aryl;

$\text{R}_3$  is  $\text{C}_1$ - $\text{C}_{10}$ alkylene,  $\text{C}_6$ - $\text{C}_{10}$ -arylene, -alkylarylene or -arylalkylene;

M is magnesium, calcium, aluminium, zinc, melamine or a condensation product of melamine,

m is 1, 2 or 3;

n is 1 or 3 and

x is 1 or 2.

M is preferably Zn, Al, melamine, melam or melem, especially Zn or Al. Aryl and arylene, alkylarylene and arylalkylene include, *inter alia*, phenyl, naphthyl, tolyl, xylyl, ethylphenyl, mesityl, propylphenyl or tert-butylphenyl and phenylene, naphthylene, methylphenylene, ethylphenylene or tert-butylphenylene, methylnaphthylene, ethylnaphthylene, tert-butyl-naphthylene, phenylmethylene, phenylpropylene and the corresponding tolyl and xylyl analogues.

Special emphasis should accordingly be given to flame retardants and flame-retarded polymer compositions according to the invention that comprise as further flame retardant active ingredient (component C) at least one such ingredient from the classes of antimony compounds, metal oxides or hydroxides, nanocomposites, mineral earths, modified mineral earths, organic or inorganic silicon compounds, titanates, zirconates, metal borates, phosphorus compounds, sterically hindered alkoxyamine compounds and/or organohalogen compounds, for example those wherein component C is at least one from the classes antimony compounds, sterically hindered alkoxyamine compounds, phosphorus compounds or/and organohalogen compounds. Especially suitable as component C are a phosphate, phosphate ester, phosphonate, phosphinate, phosphine, phosphine oxide, phosphite or/and phosphazene, more especially a metal salt or melamine (including condensation products thereof) salt of a phosphinic acid of formulae X or/and XI.

The Examples that follow illustrate the invention further.

### Examples 1-3

#### 1. Components used

Commercially available polymers (granules):

polyamide 6 (PA 6):

®Akulon K122 (DSM Engineering Plastics).

polyamide 6.6 (PA 6.6):

®Akulon S222 (DSM Engineering Plastics).

Glass fibres: standard glass fibres for polyamide, diameter 10 µm, length 4.5 mm.

Flame retardant components (in powder form):

Component A:

aluminium salt of methyl methyl phosphonic acid, hereinafter referred to as AIMMP. The compound was prepared in accordance with the procedure of EP-B-245 205, Example 2 (page 5).

Component B:

Melapur<sup>®</sup> 200 (melamine polyphosphate) from Ciba Specialty Chemicals Inc., hereinafter referred to as M200.

Component C:

aluminium salt of diethyl phosphinic acid, hereinafter referred to as DEPAL.

## 2. Preparation, processing and testing of the flame-retarding polymer compositions:

The flame retardant components are mixed with the polymer granules in the ratio indicated in the Table and, using a Haake kneader, are homogenised at a temperature of 260°C at 300 revolutions per minute and then extruded. The polymer extrudate obtained is drawn off, cooled in air and then granulated.

After being sufficiently dried, the granules are processed, using an injection moulding machine, at a mass temperature of 260°C to form test specimens having a thickness of 1.6 mm and, using the UL94 test (Underwriter Laboratories), they are tested for flame resistance and classified. The results obtained are given in the following Table.

Table

	Example 1	Example 2	Example 3
PA 6	50		50
PA 66		50	
AIMMP	11	11	8.33
M200	11	11	8.33
Glass fibres	28	28	25
DEPAL			8.33
Result of UL94 test	V0	V0	V0

The figures in the Table indicate parts by weight.

The results show that the flame retardant combinations according to the invention impart outstanding flame resistance to the polymers tested (V0 is the best flammability class according to the UL94 test).